

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 67/04, 33/06, C08J 3/00, H01J 29/28	A1	(11) International Publication Number: WO 99/35192 (43) International Publication Date: 15 July 1999 (15.07.99)
(21) International Application Number: PCT/US99/00487 (22) International Filing Date: 8 January 1999 (08.01.99) (30) Priority Data: 60/070,837 9 January 1998 (09.01.98) US (71) Applicant: METABOLIX, INC. [US/US]; 303 Third Street, Cambridge, MA 02142 (US). (72) Inventors: HOROWITZ, Daniel, M.; Apartment No. 206, 435 Washington Street, Somerville, MA 02143 (US). BRENAN, Elaine, M.; 113 Josephine Avenue, Somerville, MA 02144 (US). (74) Agents: PABST, Patrea, L. et al.; Arnall Golden & Gregory, LLP, 2800 One Atlantic Center, 1201 West Peachtree Street, Atlanta, GA 30309-3450 (US).		(81) Designated States: AU, CA, JP, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMER COMPOSITIONS PROVIDING LOW RESIDUE LEVELS AND METHODS OF USE THEREOF (57) Abstract Polymer emulsion compositions presenting low levels of residue after thermolytic decomposition are provided. The compositions, based on polyhydroxyalkanoates or acrylics, are useful in a variety of applications, including the metallization of cathode ray tube phosphor screens, where use of the compositions provides enhanced luminosity and ease of manufacture. Other applications include use of the emulsion in additives used in powder molding techniques and in the manufacture of ceramic tiles.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Background Of The Invention

It is a common practice in the manufacture of cathode ray tubes (CRTs) to apply a reflective metal coating on the inside of the phosphor screen, where the metal coating reflects light from the phosphors through the front of the CRT, thereby improving screen brightness and avoiding undesirable light scattering by the CRT funnel assembly. The metal coating ordinarily is a thin layer of aluminum applied by vapor deposition.

In order to form a reasonably flat and reflective metal coating, it is necessary to form a smooth surface over the phosphor particles before application of the metal coating. Frequently, a smooth surface is achieved by applying a temporary polymer layer that is removed after application of the metal layer. Complete removal of the polymer layer, or substrate, is essential for a bright, stable, and high quality screen image.

In one method, a smooth surface can be formed by wetting the inner surface of the phosphor screen, applying an organic solution of a volatilizable polymer, and then evaporating the organic solvent to form a thin polymer film. After the film is dried, a metal, such as aluminum, is deposited onto the surface of the polymer film, and then the entire assembly is baked to volatilize the polymer. While the method gives satisfactory results, the required use of large volumes of organic solvents is undesirable, due to the risk of fire and worker or environmental exposure.

1

filming temperature. Evaporation of the water yields a smooth polymer substrate, which is largely, but incompletely, volatilized by thermal treatment following metallization of the screen. U.S. Patent No. 3,067,055 to Saulnier Jr., for example, discloses a general method for metallization of phosphor
5 screens using aqueous polymer emulsions. U.S. Patent No. 3,582,289 to Elmes; U.S. Patent No. 3,582,390 to Saulnier; U.S. Patent No. 4,123,563 to Mitobe et al.; U.S. Patent No. 4,590,092 to Giancaterini et al.; U.S. Patent No. 4,954,366 to Pezzulo et al.; and U.S. Patent No. 5,178,906 to Patel et al. disclose additives which are used in concert with the aqueous emulsions to
10 reduce blistering and/or to improve adhesion or other properties of the metallic layer.

The emulsions used for phosphor screen metallization typically are based on acrylic resins, since these polymers depolymerize or otherwise form volatile substances at temperatures below 450 °C, the maximum
15 temperature tolerated by the glass panel. Acrylic emulsion compositions, or lacquers, are available with a variety of film-forming temperatures, hardnesses, and particle size distributions, spanning the range of properties that are known to be useful in the metallization of CRT phosphor screens. A commonly used commercial acrylic emulsion is RhoplexTM B-74 (Rohm and
20 Haas Co., Philadelphia, PA), also known as Primal B-74. The use of combinations of acrylic emulsions to enhance the quality of the metallic layer is described in U.S. Patent No. 4,284,662 to Matsuzaki et al. and U.S. Patent No. 4,990,366 to Pezzulo et al.

While the use of known aqueous-based polymer emulsions does
25 avoid the problems associated with use of organic solvent-based emulsions, the aqueous-based polymer emulsions available in the art present other disadvantages. It is generally observed that the emulsion-derived substrates do not completely bake out at temperatures up to 450 °C, rather they leave a residue or ash, which requires repeated or prolonged bake-out cycles and/or
30 oxygen supplementation in the baking atmosphere. These extra steps are undesirably costly, time-consuming, and raise additional safety issues. Furthermore, a certain quantity of residue may still remain on the phosphor

glass, reducing screen brightness.

Various efforts to overcome these deficiencies are described in the art. For example, U.S. Patent No. 5,145,511 to Patel et al. discloses a method for a combined panel bake/frit sealing cycle, which reduces the carbonaceous residue left behind on the phosphor screen by the emulsion. However, the proposed combined cycle is slower than the conventional cycle, and reduces only the carbonaceous residue, not the other residues that contribute to diminished CRT quality.

U.S. Patent No. 4,339,475 to Hinosugi et al. describes a method in which the acrylic emulsion is deposited on the phosphor screen while the screen is still wet, in order to minimize the quantity of emulsion required and thereby reduce the quantity of residue after baking-out. However, this method is difficult to use since the miscibility of the acrylic emulsion with the underlying water layer facilitates the diffusion of polymer particles into the water layer. This process results in a polymer substrate of inadequate thickness and uniformity, thereby yielding a metallic layer with diminished reflectance.

U.S. Patent No. 4,327,123 to Levine et al. describes the use of specific acrylic copolymer emulsions for phosphor screen metallization. However, the emulsions that worked suitably contained anionic surfactants, such as sodium dodecylsulfate, as well as residues from the potassium persulfate initiator. Levine disclosed that syntheses utilizing purely nonionic surfactants or no surfactants did not yield useful emulsions. The emulsions also contained inorganic initiators and/or their decomposition products. Accordingly, the emulsions do not significantly improve over other conventional materials, such as Rhoplex™ B-74, available from Rohm & Haas.

PCT application WO 96/17369 by Adebayo et al. discloses the use of an emulsion of a poly(hydroxyalkanoate) copolymer, poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV or Biopol™), for metallization of a phosphor screen. However, due to its bacterial origin, PHBV emulsion contains biological residues that are nonvolatilizable and

cause charring or discoloration after bake-out when this emulsion is used for CRT metallization. Accordingly, the existing emulsion techniques are unsuitable for use in producing CRTs for applications demanding superior brightness, such as high-definition television (HDTV).

5 It is therefore an object of this invention to provide aqueous polymer compositions for use in manufacturing processes with reduced levels of residue following their thermolytic removal.

 It is another object of this invention to provide aqueous polymer emulsion compositions and methods of preparing and using these emulsions,
10 which can be used to produce CRTs having enhanced luminosity.

Summary Of The Invention

 Polymer emulsion compositions containing low levels of residue after thermolytic decomposition are provided. The emulsions are aqueous
15 emulsions including polyhydroxyalkanoate and/or acrylic polymers, and can be prepared from commercially available emulsions which are treated to remove non-volatilizable components. The removal process preferably includes filtration and/or centrifugation techniques, and optionally can be conducted in the presence of additives known to be volatilizable under
20 manufacturing conditions, such as in the making of cathode ray tubes (CRTs). Methods for preparing these emulsion compositions are described.

 The polymer emulsions are useful in a variety of applications, especially in the metallization of phosphor screens of CRTs, where use of the emulsion yields enhanced CRT luminosity and provides improved ease of
25 manufacture. In a preferred embodiment, the method for metallizing a phosphor screen includes the steps of (a) coating the phosphor screen with the polymer emulsion composition described herein; (b) drying the composition to form a polymer substrate; (c) applying a reflective metallic layer to the substrate to form a metallized phosphor screen; and (d) baking
30 the metallized phosphor screen to volatilize the substrate, leaving the reflective metallic layer intact on the phosphor screen.

 Other applications include use of the emulsion in additives used in

powder molding techniques and in the manufacture of ceramic tiles.

Detailed Description Of The Invention

In a typical process for making acrylic emulsions, a surfactant-
5 stabilized emulsion of one or more monomers in water is prepared, one or
more radical initiators are added, and the polymerization reaction is allowed
to proceed, optionally with addition of extra monomer. Polymerization
generally is viewed as occurring within surfactant micelles, to which
additional monomers are transferred by diffusion from the monomer
10 droplets. The initiators are generally combinations of sulfur-containing
species, such as inorganic salts of persulfate and metabisulfite.
The polymer particle size in the resulting emulsion is governed by a variety
of factors. A critical factor is the nature and concentration of the surfactants
present. To maintain the small particle size and uniform size distribution
15 required for use as a lacquer for CRT phosphor screens, anionic surfactants
are required during acrylic polymerization, with the optional addition of
nonionic surfactants. Examples of such anionic surfactants include sodium
dodecylsulfate, sodium alkylbenzenesulfonate, and sodium
dioctylsulfosuccinate. It has been discovered, however, that anionic
20 surfactants, as well as inorganic, sulfur-containing residues from the radical
initiators, have poor bake-out characteristics under thermolytic
manufacturing processes, such as the metallization of CRT phosphor screens.
Accordingly, emulsion compositions were prepared from which these non-
volatilizable substance are largely removed and which leave essentially no
25 residue during thermolytic removal, for example, in the metallization of CRT
screens and as a binder in the fabrication of molded products such as ceramic
tiles.

As used herein, the term "non-volatilizable" refers to a substance
which, upon heating in air to a temperature of 450 °C for an interval of not
30 longer than 45 minutes, leaves a solid residue of greater than 2% by weight.
Determination of volatilizability may be conducted either using the
substance in the neat state or using a solution or suspension of the substance

in solvent.

I. Polymer Emulsion Compositions

The principal component of the present compositions is an aqueous emulsion of a polymer, preferably an acrylic, polyhydroxyalkanoate, or mixture thereof. The composition should be substantially free of non-volatilizable substances, but can include volatilizable additives.

1. Acrylics

Known acrylic emulsion compositions can be used if treated as described herein to remove non-volatilizable substances. Acrylic emulsions are manufactured by methods well known in the art of polymer synthesis (Gilbert, R.G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London, 1995). Acrylics useful in the compositions described herein include ones having units of formula:



wherein R^1 and R^2 are any radical of formula $\text{C}_n\text{H}_{2n+1}$ and wherein n is an integer from 0 to 10.

A preferred acrylic Rhoplex™ B-74. Other useful acrylic polymers are disclosed, for example, in U.S. Patent No. 3,067,055 to Saulnier.

2. Polyhydroxyalkanoates

In another embodiment, the composition includes an emulsion or latex of a biological poly(hydroxyalkanoate) (PHA). Since emulsions prepared using known treatments of medium-chain length PHAs (de Koning, G.J.M.; Witholt, B. *Bioprocess Eng.* **1997**, *17*, 7-13; de Koning, G.J.M.; Kellerhals, M.; van Meurs, C.; Witholt, B. *Bioprocess Eng.* **1997**, *17*, 15-21), contain non-volatilizable substances for use as thermolyzable lacquers or binders, these emulsions must be processed, as described herein, to remove non-volatilizable substances.

Several types of PHAs are known. It is useful to broadly divide the PHAs into two groups according to the length of their side chains and according to their pathways for biosynthesis. Those with short side chains, such as polyhydroxybutyrate (PHB), a homopolymer of R-3-hydroxybutyric acid units, are crystalline thermoplastics; PHAs with long side chains are

more elastomeric. The former polymers have been known for about seventy years (Lemoigne & Roukhelman 1925), while the latter polymers are a relatively recent discovery (deSmet, *et al.*, *J. Bacteriol.*, **154**:870-78 (1983)). Before this designation, however, PHAs of microbial origin containing both R-3-hydroxybutyric acid units and longer side chain units from C5 to C16 were identified (Wallen & Rowheder, *Environ. Sci. Technol.*, **8**:576-79 (1974)). A number of bacteria which produce copolymers of D-3-hydroxybutyric acid and one or more long side chain hydroxyacid units containing from five to sixteen carbon atoms have been identified more recently (Steinbuchel & Wiese, *Appl. Microbiol. Biotechnol.*, **37**:691-97 (1992); Valentin *et al.*, *Appl. Microbiol. Biotechnol.*, **36**: 507-14 (1992); Valentin *et al.*, *Appl. Microbiol. Biotechnol.*, **40**:710-16 (1994); Abe *et al.*, *Int. J. Biol. Macromol.*, **16**:115-19 (1994); Lee *et al.*, *Appl. Microbiol. Biotechnol.*, **42**:901-09 (1995); Kato *et al.*, *Appl. Microbiol. Biotechnol.*, **45**:363-70 (1996); Valentin *et al.*, *Appl. Microbiol. Biotechnol.*, **46**:261-67 (1996); U.S. Patent No. 4,876,331 to Doi). Useful examples of specific two-component copolymers include PHB-co-3-hydroxyhexanoate (Brandl *et al.*, *Int. J. Biol. Macromol.*, **11**:49-55 (1989); Amos & McInerney, *Arch. Microbiol.*, **155**:103-06 (1991); U.S. Patent No. 5,292,860 to Shiotani *et al.*). Chemical synthetic methods have also been applied to prepare racemic PHB copolymers of this type for applications testing (WO 95/20614, WO 95/20615, and WO 96/20621).

A. Polymer Formulas

Suitable molecular weights of the polymers are between about 10,000 and 4 million Daltons. Preferable molecular weights are between about 50,000 and 1.5 million Daltons. The PHAs preferably contain one or more units of the following formula:



wherein n is 0 or an integer; and

wherein R¹, R², R³, and R⁴ are independently selected from saturated and unsaturated hydrocarbon radicals, halo- and hydroxy- substituted radicals, hydroxy radicals, halogen radicals, nitrogen-substituted radicals,

oxygen-substituted radicals, and hydrogen atoms.

Suitable monomeric units include hydroxybutyrate, hydroxyvalerate, hydroxyhexanoate, hydroxyheptanoate, hydroxyoctanoate, hydroxynonanoate, hydroxydecanoate, hydroxyundecanoate, and hydroxydodecanoate units. PHAs including monomers and polymers and derivatives of 3-hydroxyacids, 4-hydroxyacids and 5-hydroxyacids can be used. Representative PHAs are described in Steinbüchel & Valentin, *FEMS Microbiol. Lett.*, **128**:219-28 (1995).

B. Preparation of Polyhydroxyalkanoates

10 The PHAs can be prepared from a biological source such as a microorganism which naturally produces the PHAs or which can be induced to produce the PHAs by manipulation of culture conditions and feedstocks, or microorganisms or a higher organism such as a plant, which has been genetically engineered so that it produces PHAs.

15 Methods which can be used for producing PHA polymers from microorganisms which naturally produce polyhydroxyalkanoates are described in U.S. Patent No. 4,910,145 to Holmes, et al.; Byrom, "Miscellaneous Biomaterials" in *Biomaterials* (Byrom, ed.) pp. 333-59 (MacMillan Publishers, London 1991); Hocking and Marchessault, 20 "Biopolyesters" in *Chemistry and Technology of Biodegradable Polymers* (Griffin, ed.) pp. 48-96 (Chapman & Hall, London 1994); Holmes, "Biologically Produced (R)-3-hydroxyalkanoate Polymers and Copolymers" in *Developments in Crystalline Polymers* (Bassett, ed.) vol. 2, pp. 1-65 (Elsevier, London 1988); Lafferty *et al.*, "Microbial Production of 25 Poly-b-hydroxybutyric acid" in *Biotechnology* (Rehm & Reed, eds.) vol. 66, pp. 135-76 (Verlagsgesellschaft, Weinheim 1988); Müller & Seebach, *Angew. Chem. Int. Ed. Engl.* **32**:477-502 (1993).

Methods for producing PHAs in natural or genetically engineered organisms are described by Steinbüchel, "Polyhydroxyalkanoic Acids" in 30 *Biomaterials* (Byrom, ed.) pp. 123-213 (MacMillan Publishers, London 1991); Williams & Peoples, *CHEMTECH*, **26**:38-44 (1996); Steinbüchel & Wiese, *Appl. Microbiol. Biotechnol.*, **37**:691-97 (1992); U.S. Patent Nos.

- 5,245,023; 5,250,430; 5,480,794; 5,512,669; 5,534,432 to Peoples and Sinskey; Agostini *et al.*, *Polym. Sci.*, Part A-1, 9:2775-87 (1971); Gross *et al.*, *Macromolecules*, 21:2657-68 (1988); Dubois, *et al.*, *Macromolecules*, 26:4407-12 (1993); Le Borgne & Spassky, *Polymer*, 30:2312-19 (1989);
- 5 Tanahashi & Doi, *Macromolecules*, 24:5732-33 (1991); Hori *et al.*, *Macromolecules*, 26:4388-90 (1993); Kemnitzer *et al.*, *Macromolecules*, 26:1221-29 (1993); Hori *et al.*, *Macromolecules*, 26:5533-34 (1993); Hocking & Marchessault, *Polym. Bull.*, 30:163-70 (1993); Xie *et al.*, *Macromolecules*, 30:6997-98 (1997); and U.S. Patent No. 5,563,239 to
- 10 Hubbs *et al.* Other polymer synthesis approaches including direct condensation and ring-opening polymerization of the corresponding lactones are described in Jesudason & Marchessault, *Macromolecules* 27:2595-602 (1994); U.S. Patent No. 5,286,842 to Kimura; U.S. Patent No. 5,563,239 to Hubbs *et al.*; U.S. Patent No. 5,516,883 to Hori *et al.*; U.S. Patent No.
- 15 5,461,139 to Gonda *et al.*; and Canadian Patent Application No. 2,006,508. WO 95/15260 describes the manufacture of PHBV films, and U.S. Patent Nos. 4,826,493 and 4,880,592 to Martini *et al.* describe the manufacture of PHB and PHBV films. U.S. Patent No. 5,292,860 to Shiotani *et al.* describes the manufacture of the PHA copolymer poly(3-hydroxybutyrate-co-3-
- 20 hydroxyhexanoate.

3. *Surfactants and Other Additives*

- Polymer emulsions typically are supplemented with functional additives, such as surfactants, pH control agents, solvents, inorganic salts, chelators, dispersants, emulsifiers, film-forming agents, coalescing agents,
- 25 wetting or leveling aids, antifoaming agents, defoaming agents, biocides, stabilizers, preservatives, viscosity modifiers, rheological control agents, and plasticizers. The additives may be incorporated before, during, or after polymerization, and can contribute additional residue following thermolytic removal of the polymer. In the emulsion compositions disclosed herein, it is
- 30 desirable to remove or avoid using non-volatilizabile additives.

Determination of volatilizability may be conducted either using the substance in the neat state or using a solution or suspension of the substance

in solvent.

II. Methods of Preparing the Emulsion Compositions

Preparation of the emulsion compositions includes separation of the non-volatilizable constituents. The separation can be conducted using one or more of several techniques, including micro- or ultra-filtration, dialysis, and centrifugation. In all preparative methods, it is desirable to maintain the working temperature below the minimum filming temperature of the emulsion, as this reduces fouling of filters, membranes, and equipment and prevents coalescence of the polymer particles. It may also be useful in the preparation process to add an adequate quantity of a volatilizable surfactant, emulsifier, or dispersant, in order to maintain the quality of the emulsion during processing.

Without being limited by the theory, it is believed that non-volatilizable detergents needed for the preparation of the emulsion from a bacterial cell suspension become adsorbed to the particle surface, from which they may only be displaced by treatment with a relative excess of another surface active agent.

1. *Filtration and Diafiltration*

In one embodiment, a commercial emulsion, such as Rhoplex™ B-74, is processed by micro- or ultra-filtration, whereby non-volatilizable, water-soluble or water-dispersible substances are washed from the emulsion. The washed emulsion optionally can be supplemented with volatilizable functional additives, before, during, or after the filtration. (To add before washing, the additives should be of a type, like Hypermer™, which are tightly adsorbed to polymer particles and do not readily wash away.)

In another preferred embodiment, the emulsion is processed by diafiltration using a tangential flow apparatus equipped with a ceramic membrane element of carefully chosen pore size. A suitable membrane element should readily pass an aqueous solution comprising non-volatilizable substances, including any micelles or aggregates of the same substance, while retaining most of the polymer particles. A diafiltration process is described in Examples 2-4 below. Washing may be effected with

particular efficiency by (a) diluting the starting emulsion to a solids concentration where the performance of the filter element is improved (b) washing the emulsion by diafiltration using one or more volumes of water or an aqueous solution containing volatilizable additives (c) concentrating the washed emulsion to a solids concentration appropriate for transportation.

2. *Centrifugation*

In another preferred embodiment, the emulsified PHA particles are centrifuged and resuspended one or more times in the presence of an aqueous solution of a volatilizable surfactant, which results in a significant reduction in the residue following thermal treatment of the emulsion. A centrifugation process is described below in Example 5.

Filtration or dialysis can be used in lieu of centrifugation and resuspension. For example, an emulsion including polymer particles and non-volatilizable substances can be placed on one side of a dialysis membrane (e.g., a cellulosic membrane), while the membrane is contacted (e.g. on the other side) with water or an aqueous solution that includes selected volatilizable additives. Polymer particles are retained on the membrane, and the non-volatilizable substances are removed and/or replaced with volatilizable additives.

3. *Auxiliary Treatments*

In preparing certain of the emulsion compositions disclosed herein, it may be beneficial to perform additional preparation steps to enhance the performance of the compositions. For example, it is known that, when persulfate is used to initiate a polyolefin emulsion polymerization, a sulfur-containing moiety may be covalently incorporated into the polymer at the chain terminus. As this sulfur-containing moiety may also be a source of undesirable residue during phosphor screen bake-out, it may be advantageous to effect its removal during processing. Accordingly, in one embodiment, the emulsion is treated with an alkaline solution prior to or during filtration, centrifugation, or dialysis, to effect the hydrolysis of the sulfate ester linkage and the solubilization of this moiety. The alkaline solution should be selected such that hydrolysis of any oxygen esters present

in the polymer is minimized. The removal of a substantial majority of the non-volatilizable impurities can, however, be effected using the methods described herein whether or not the alkali treatment is performed.

A slight degradation of the emulsion quality may occur due to shearing, skinning, coalescence, aggregation, flocculation, or other processing factors, irrespective of the method selected for removal of non-volatilizable components. This degradation generally is manifested by the appearance of a subpopulation of polymer particles having a significantly higher particle size than the bulk of the particles. Such large particles are known to be deleterious to film formation and quality in film-forming polymer emulsions. Accordingly, in one embodiment of the methods and compositions described herein, the larger particles are substantially removed from the processed emulsion by centrifugation or filtration. For film-forming applications, particles with the largest dimension over 10 μm , and especially those with the largest dimension over 50 μm , generally are considered undesirable, and should be removed.

III. Methods of Using the Emulsion Compositions

The emulsion compositions described herein are useful in several applications, including the metallization of phosphor screens and in powder molding processes.

1. Metallization of Phosphor Screens

In the preferred embodiment, the method for phosphor screen metallization employs known techniques, such as described in the background section above, using emulsion compositions described herein. The compositions described herein provide improved metallization of CRT phosphor screens following a single bake-out cycle at 450 °C. Moreover, the improvement should be evident regardless of the specific method of applying the emulsion or the nature and number of the subsequent heating cycles, since unlike conventional emulsions used as phosphor screen lacquers, the present compositions are rendered essentially free of non-volatilizable substances. Accordingly, use of the compositions should permit one to reduce the temperature, duration, and severity of the bake-out stage, and

increase its effectiveness to yield a brighter, more durable CRT.

In a preferred embodiment, the emulsion is formulated to a solids content of 15-30% (wt./wt.), and is applied to the phosphor screen at a temperature near the minimum filming temperature for the emulsion.

- 5 Following drying and metallization, the emulsion components are thermolytically removed (e.g., burned out), for example, by firing in a furnace or similar device, at a temperature of approximately 450°C or less. Essentially complete removal of the polymer substrate can be accomplished using this process. Moreover, due to the relative ease of the bake-out
- 10 process, the removal can be achieved during the thermal sealing of the CRT funnel assembly to the phosphor screen, without a separate pre-bake of the front panel.

2. *Powder Processing*

- In a related application, the emulsion compositions can be utilized as
- 15 aids in powder processing, such as in the manufacture of ceramic or metallic forms from powders, where the emulsions can be used as binders, lubricants, or agglomerators for the constituent powders. It is generally desirable to remove these additives after forming the appropriate shapes, for example during firing in the sintering of the ceramic or metallic green forms. Certain
- 20 polymer emulsions known in the art are undesirable for use in these applications, since they release sulfur-containing fumes at the high processing temperatures typical of ceramic sintering, and/or they leave a residue that is detrimental to the look or performance of the finished ceramic or metallic forms. The compositions described herein can be used to reduce
- 25 or avoid these problems due to the composition's low sulfur content and low ash residue.

- In a preferred embodiment, the acrylic compositions disclosed herein are used to replace acrylics used in the manufacture of ceramic tiles, which release sulfur-containing fumes, which are an environmental and health
- 30 hazard.

In another embodiment, the polyhydroxyalkanoate (PHA) compositions are used to replace or augment the binders used in ceramic or

metallic molding compositions. The PHA molding compositions can be used in forming techniques known in the art, such as slip casting, tape casting, extrusion, injection molding, dry pressing and screen printing. These and other powder processing techniques are described in German, "Powder Injection Molding," (Metal Powder Industries Federation, Princeton, New Jersey 1990) and German and Bose, "Injection Molding of Metals and Ceramics," (Metal Powder Industries Federation, Princeton, New Jersey 1997). Examples of products that can be made using the compositions disclosed herein include ceramic tiles, combustion engine parts, valves, rotors, gear assemblies, printed circuit boards, and superconductors.

The compositions and methods of preparation and use thereof described herein are further described by the following non-limiting examples.

**Example 1: Determination of Unvolatilized Residue
For Emulsions and Additives**

Dry samples (0.2-1.0 g) were heated in air to 450 °C at a rate of 10 °C/min. in quartz or aluminum vessels. The furnace temperature was maintained at 450 °C for a period of 45 min., after which the samples were allowed to cool down and the unvolatilized residue weighed. Liquid samples containing water (solids content 0.2-1.0 g) were heated in air to 150 °C at a rate of 10 °C/min., and maintained at 150 °C for 30 min. to evaporate the water. Next, the temperature was increased to 450 °C at a rate of 10 °C/min., and maintained at 450 °C for a period of 45 min. The samples then were cooled and weighed. The unvolatilized residue was reported as a percentage of the weight of solids present in the original sample.

Using this procedure, the following additives were determined to yield an unvolatilized residue of less than 0.5% by weight, based on the weight of solids present: HypermerTM CG-6 (available from ICI Surfactants), alkylphenol ethoxylates (Makon series, available from Stepan Co.), MakonTM NF12 (available from Stepan Co.), alkylamine-*N*-oxides (Ammonyx LO and SO, available from Stepan Co.), AbexTM 26S (available

from Rhone-Poulenc), Triton™ DF-16 (available from Sigma Chemical), Triton™ X-100 (available from Sigma Chemical), polyoxyethylene esters (Myrj™ series, available from ICI Surfactants), polyoxyethylene ethers (Brij™ series, available from ICI Surfactants), Surfynol™ 420 (available
5 from Air Products), Troysan™ 174 (available from Troy Co.), Canguard™ 442 (available from Angus Chemical Co.), and glutaraldehyde (available from Union Carbide).

Using the same procedure, the following substances were determined to yield an unvolatilized residue of greater than 2.0% by weight, based on the
10 weight of solids present: sodium alkylbenzenesulfonate, sodium dodecylsulfate, EDTA, diethylenetriaminepentaacetic acid, protein, nucleic acid, fatty acids, and bacterial cell wall components.

The same procedures for quantifying unvolatilized residues were used in the following examples.

15

**Example 2: Preparation of Novel Acrylic Emulsions
by Polymeric Membrane Filtration**

Rhoplex™ B-74 emulsion (Rohm & Haas, 38% solids wt./wt.) was diluted 1:3 with deionized water to a solids content of approximately 9%
20 (wt./wt.). Hypermer CG-6 was added to the emulsion to an active concentration of 0.5% (wt./vol.), and the pH was adjusted to 7 with ammonium hydroxide. The sample (0.4 L) was processed by diafiltration using a benchtop hollow-fiber cross-flow filtration unit (A/G Technology QuixStand) equipped with a 500 kDa nominal cutoff ultrafiltration
25 membrane (A/G Technology, 0.05 m² membrane area). The emulsion was maintained at an approximately constant volume by continuous addition of a solution of 0.5% (wt./vol.) Hypermer CG-6 in deionized water. After 10 volumes of diafiltration, the unvolatilized residue from the emulsion was reduced from about 1% (by weight of the solids present) to an undetectable
30 level, which was less than 0.1 %. Similar results were obtained using Makon 12 or Myrj 52 surfactants in place of Hypermer CG-6, and using deionized water alone. In the latter case, however, it was necessary to add a

volatilizable surfactant at the end of the process in order to obtain an emulsion with satisfactory wetting properties.

**Example 3: Preparation of a Novel Acrylic Emulsion
by Ceramic Membrane Filtration**

5 Rhoplex™ 74 emulsion (Rohm & Haas, 38% solids wt./wt.) was diluted 1:3 with deionized water to a solids content of approximately 9% (wt./wt.). Hypermer CG-6 was added to the emulsion to an active concentration of 0.5% (wt./vol.), and the pH was adjusted to 7 with
10 ammonium hydroxide. The sample was processed by diafiltration using a pilot scale ceramic microfiltration unit (Niro Filtration) equipped with a 0.1 µm nominal cutoff microfiltration element (U.S. Filter Corp. Membralox series, 0.2 m² membrane area). The emulsion was maintained at an approximately constant volume by continuous addition of a solution of 0.5%
15 (wt./vol.) Hypermer CG-6 in deionized water. After 10 volumes of diafiltration, the unvolatilized residue from the emulsion was reduced from about 1% (by weight of the solids present) to an undetectable level, which was less than 0.1%. Elemental analysis showed that the dried solids from untreated Rhoplex™ B-74 had a sulfur content of 0.46% by weight, and that
20 solids from the final, treated product contained only 0.049% S, which is a reduction of 89% in the sulfur content.

**Example 4: Preparation of a Novel Acrylic Emulsion
by Ceramic Membrane Filtration**

25 Rhoplex™ B-74 emulsion (Rohm & Haas, 38% solids wt/wt) was diluted 1:3 with deionized water to a solids content of approximately 9% (wt./wt.). Water-soluble nonylphenol ethoxylate (Makon 12, Stepan Co.) was added to the emulsion to an active concentration of 0.5% (wt./vol.), and the pH was adjusted to 7 with ammonium hydroxide. The sample was
30 processed by diafiltration using the pilot scale ceramic microfiltration unit described in Example 3 above. The emulsion was maintained at an approximately constant volume by continuous addition of a solution of 0.5%

(wt./vol.) Makon 12 in deionized water. After 7 volumes of diafiltration, addition of Makon 12 solution was discontinued and the emulsion was concentrated by filtration to a solids concentration of 29% (wt./wt.). This emulsion had a viscosity of 25 cP. The unvolatilized residue from this
5 emulsion was 0.12% (by weight of the solids presents), while that for untreated RhoplexTM B-74 was 0.79%, which is a reduction of 85% in the amount of unvolatilized residue.

Example 5: Centrifugal Classification of an Acrylic Emulsion

10 An emulsion was prepared as in Example 4 above with a solids content of 29.12% (wt./wt.). It contained a minor fraction of large particles having an approximate size of 1-100 μ m. The bulk of the particles appeared to be in the 70 nm size range. The emulsion was centrifuged in a Sorvall centrifuge for 30 min. at 14,000 g. The centrifuge cake, which was
15 subsequently discarded, contained 0.6% by weight of the total solids originally present, and had a median particle size of 2.5 μ m and a particle size range from 0.1 to 183 μ m, according to a Coulter LS130 particle size analyzer. The supernatant, which was retained, was essentially free of particles greater than 1 μ m in diameter and had a solids content of 28.95%
20 (wt./wt.).

Example 6: Preparation of a PHA Emulsion

A PHA emulsion was made and purified from bacterial cells of *Pseudomonas putida* cultivated on octanoic acid, using known methods.
25 Upon heating, the emulsion provided an unvolatilized residue of 1.71% (by weight of the solids present), which was significantly higher than that of the commercial RhoplexTM B-74 emulsion. Samples of the emulsion (6.4% solids wt./wt.) were centrifuged for 45 min. at 50,000 g. Each pellet was resuspended to its original volume in a solution of a volatilizable surfactant,
30 recentrifuged as above, and then resuspended in a small volume of deionized water. The percentage of unvolatilized residues for emulsions prepared with several different surfactants is shown in Table 1 below. The emulsion

prepared using the Ammonyx LO was used to coat a CRT phosphor screen, which was subsequently metallized and baked-out with satisfactory results.

TABLE 1: Unvolatilized Residues Using PHA with Various Surfactants

Surfactant	% Unvolatilized Residue*	% Residue Reduction
none	0.43	75
Triton X-100	0.38	78
Makon 12	0.45	74
Brij 35	0.41	76
Brij 76	0.42	75
Ammonyx LO	0.19	89

* by weight of the solids present

We claim:

1. A composition comprising an aqueous emulsion of a polymer selected from the group consisting of (i) acrylics having units of formula:



wherein R^1 and R^2 are any radical of formula $\text{C}_n\text{H}_{2n+1}$

and wherein n is an integer from 0 to 10;

(ii) polyhydroxyalkanoates; and mixtures thereof,

wherein the emulsion is prepared to render the emulsion substantially free of non-volatilizable substances.

2. The composition of claim 1 wherein the mass of unvolatilized residue remaining after heating the prepared emulsion to 450 °C is less than 20% of the mass of the residue remaining after heating the emulsion to 450 °C.

3. The composition of claim 1 wherein the mass of unvolatilized residue remaining after heating the prepared emulsion to 450 °C is less than 0.2% of the mass of solids present in the prepared emulsion.

4. The composition of claim 1 wherein the mass of sulfur is less than 0.1% of the mass of solids present in the emulsion.

5. The composition of claim 1 wherein the minimum filming temperature is between about 40 °C and 60 °C.

6. The composition of claim 1 wherein the median particle size of solids in the prepared emulsion is less than 0.1 μm .

7. The composition of claim 1 further comprising volatilizable additives selected from the group consisting of pH control agents, solvents, chelators, surfactants, dispersants, emulsifiers, film-forming agents, coalescing agents, wetting aids, leveling aids, antifoaming agents, defoaming agents, biocides, stabilizers, preservatives, viscosity modifiers, rheological control agents, plasticizers, and drying aids.

8. The composition of claim 7 wherein the volatilizable additive is selected from the group consisting of ammonia, organic amines, alkylphenol ethoxylates, alkylamine oxides, ethoxylated alcohols,

ethoxylated fatty acids, graft copolymers of an acrylate resin with poly(oxyethylene), copolymers of poly(oxyethylene) and poly(oxypropylene), and acetylenic diols.

9. The composition of claim 1 further comprising a modifier to improve properties of a metallized cathode-ray tube phosphor screen formed in a process using the composition.

10. The composition of claim 9 wherein the modifier is selected from the group consisting of adhesion-promoters, pore-forming agents, and anti-blistering agents.

11. The composition of claim 10 wherein the modifier is selected from the group consisting of hydrogen peroxide, colloidal silica, soluble silicates, ammonium oxalate, ammonium tetraborate, poly(vinyl alcohol), boric acid complexes of poly(vinyl alcohol), water-soluble polymers, and water-dispersible polymers.

12. A method for making a composition comprising an aqueous emulsion of a polymer substantially free of non-volatilizable substances, the method comprising:

(a) preparing an aqueous emulsion of a polymer selected from the group consisting of (i) acrylics having units of formula:



wherein R^1 and R^2 are any radical of formula $\text{C}_n\text{H}_{2n+1}$

and wherein n is an integer from 0 to 10,

(ii) polyhydroxyalkanoates, and mixtures thereof, wherein the emulsion contains non-volatilizable substances; and

(b) removing substantially all of the non-volatilizable substances from the emulsion.

13. The method of claim 12 wherein the non-volatilizable substances are removed using a micro- or ultra-filtration process in which polymer particles are maintained in a dispersed state by addition of an aqueous solution to the retentate of the filtration process.

14. The method of claim 13 wherein the filtration process utilizes a filter element formed from a ceramic or polymeric substance, and wherein

the performance of the filter is maintained by tangential flow of the retentate.

15. The method of claim 12 wherein the non-volatilizable substances are removed using a centrifugation process.

16. The method of claim 15 wherein polymer solids are collected as the heavier phase in the centrifugation process, and then are resuspended in an aqueous solution containing volatilizable additives.

17. The method of claim 12 wherein the non-volatilizable substances are removed using a liquid-liquid dialysis process.

18. The method of claim 12 further comprising
(c) removing solid particles formed during step (b) wherein the solid particles are larger than 1 μm in size.

19. The method of claim 12 conducted at a temperature below the minimum filming temperature of the emulsion.

20. The method of claim 12 further comprising
treating the emulsion of step (a) with an alkaline solution to solubilize sulfur-containing moieties present in the emulsion, before or during step (b).

21. A method of metallizing a phosphor screen for use in cathode-ray tube phosphor screens, the method comprising:

(a) depositing onto the phosphor screen a composition comprising an aqueous emulsion of a polymer selected from the group consisting of (i) acrylics having units of formula:



wherein R^1 and R^2 are any radical of formula $\text{C}_n \text{H}_{2n+1}$

and wherein n is an integer from 0 to 10;

(ii) polyhydroxyalkanoates; and mixtures thereof,

wherein the emulsion is substantially free of non-volatilizable substances,

(b) drying the emulsion to form a solid substrate;

(c) applying a metallic layer to the solid substrate; and

(d) volatilizing the solid substrate by thermal means.

22. The method of claim 21 wherein the emulsion has a solids

content of between about 10 and 25 % by weight of the emulsion.

23. The method of claim 21 wherein steps (a) through (c) are conducted at a temperature at approximately equal to the minimum filming temperature of the emulsion.

24. The method of claim 21 wherein the solid substrate is volatilized by heating it to a temperature of between about 300 and 450 °C.

25. The method of step 21 wherein step (d) is conducted during sealing of a funnel assembly of a cathode-ray tube to the phosphor screen.

26. A method of forming a shaped product having reduced processing additive residue, the method comprising:

(a) compounding a powdered material with a processing additive comprising an aqueous emulsion of a polymer selected from the group consisting of (i) acrylics having units of formula:



wherein R^1 and R^2 are any radical of formula $\text{C}_n \text{H}_{2n+1}$

and wherein n is an integer from 0 to 10;

(ii) polyhydroxyalkanoates; and mixtures thereof,

wherein the emulsion is substantially free of non-volatilizable substances, to form an admixture;

(b) molding the admixture to form the shaped product; and

(c) thermally decomposing the additive.

27. The method of claim 26 wherein the powdered material is selected from the group consisting of glass, ceramics, metals, alloys, and mixtures thereof.

28. The method of claim 26 wherein the processing additive is selected from the group consisting of binders, agglomerators, and lubricants.

29. The method of claim 26 wherein the method of forming shaped products is selected from the group consisting of slip casting, tape casting, extrusion, injection molding, dry pressing, and screen printing.

30. A molded article formed by a method comprising molding a composition comprising a powdered material admixed with an aqueous emulsion of a polymer selected from the group consisting of

(i) acrylics having units of formula:



wherein R^1 and R^2 are any radical of formula $\text{C}_n\text{H}_{2n+1}$

and wherein n is an integer from 0 to 10;

(ii) polyhydroxyalkanoates; and mixtures thereof,

wherein the emulsion is substantially free of non-volatilizable substances.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/00487

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 67/04, C08L 33/06, C08J 3/00, H01J 29/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08J, C08L, H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0735008 A2 (ELF ATOCHEMITALIA S.R.L.), 2 October 1996 (02.10.96), page 1 --	1-30
X	Bioprocess Engineering, Volume 17, 1997, G.J.M. de Koning et al, "A process for the recovery of poly(hydroxyalkanoates) from Pseudomonads Part 2: Process development and economic evaluation", page 15 - page 21, conclusions	1,12
A	--	3-11,13-30
A	WO 9617369 A1 (COOKSON GROUP PLC), 6 June 1996 (06.06.96), claim 1 --	1-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 May 1999

Date of mailing of the international search report

10.06.1999

Name and mailing address of the International Searching Authority
European Patent Office P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel(+31-70)340-2040, Tx 31 651 epo nl.
Fax(+31-70)340-3016

Authorized officer

BARBRO NILSSON/E1s

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/00487

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0802558 A2 (ROHM AND HAAS COMPANY), 22 October 1997 (22.10.97) -- -----	1-30

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 00487

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: **claim no. 2**
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

Because the claim is obscure.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

SA 220996

Information on patent family members

03/05/99

International application No.

PCT/US 99/00487

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0735008 A2	02/10/96	IT 1275994 B IT MI950645 A PL 313554 A US 5731378 A	24/10/97 30/09/96 14/10/96 24/03/98
WO 9617369 A1	06/06/96	AU 3932395 A DE 69507898 D EP 0795190 A,B GB 9424175 D JP 10510394 T US 5874124 A	19/06/96 00/00/00 17/09/97 00/00/00 06/10/98 23/02/99
EP 0802558 A2	22/10/97	AU 1648497 A BR 9701586 A CA 2200931 A CN 1167998 A CZ 9700964 A FR 2746959 A JP 10031959 A PL 319211 A SG 52938 A	09/10/97 23/06/98 01/10/97 17/12/97 15/10/97 03/10/97 03/02/98 13/10/97 28/09/98